

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
22 July 2004 (22.07.2004)

PCT

(10) International Publication Number
WO 2004/061020 A1

(51) International Patent Classification⁷: C09D 5/18,
C08L 25/16, 33/06

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(21) International Application Number:
PCT/IB2003/006398

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(22) International Filing Date:
19 December 2003 (19.12.2003)

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR,
CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD,
GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR,
KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN,
MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU,
SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA,
UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
02293183.6 20 December 2002 (20.12.2002) EP

(84) Designated States (*regional*): ARIPO patent (BW, GH,
GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,
ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE,
SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA,
GN, GQ, GW, ML, MR, NE, SN, TD, TG).

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Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

(54) Title: POLYMER BINDER FOR INTUMESCENT COATINGS

(57) Abstract: A copolymer for the use in or as polymeric binder in intumescent coatings, comprising a blend of a Newtonian copolymer and of a reticulated copolymer, said Newtonian and reticulated copolymers consisting of substituted styrene and substi-
tuted acrylate and comprising at least p-methylstyrene (PMS) and 2-ethylhexylacrylate (2EHA).

WO 2004/061020 A1

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1 JC05 Rec'd PCT/PTO 17 JUN 2005**Polymer binder for intumescent coatings**

5 The present invention relates to copolymers for use in or as polymeric binders for fire retardants coatings, more particularly intumescent coatings providing excellent fire proofing performance.

10 Intumescent coating compositions are well-known in the art. An outstanding feature of intumescent coatings is that they may be applied on substrates, such as metal, wood, plastics, graphite and other materials, in the manner of a coating having relatively low film thickness. Upon exposure to fire, heat or flames, the intumescent
15 coatings expand considerably in terms of thickness to produce an insulative layer of char and char foam.

 The most commonly used intumescent coatings contain four basic components, sometimes called "reactive pigments", dispersed in a binder matrix. The reactive
20 pigments include

- (1) an inorganic acid or a material which yields an acid at temperatures between 100 and 250°C, such as for example, ammonium polyphosphate which yields phosphoric acid;
- 25 (2) carbon source such as a polyhydric material rich in carbon, also referred to as a carbon hydrate, for example, pentaerythritol or dipentaerythritol;
- (3) an organic amine or amide, such as for example, a melamine; and optionally
- 30 (4) a halogenated material which releases hydrochloric acid gas on decomposition.

The basic intumescent mechanism is proposed to involve the formation of a carbonaceous char by the dehydration reaction of the generated acid with the polyhydric material. The amine may participate in char formation, but is described primarily as a blowing agent for insulating char foam formation. Because the insulating char stops fire and remains on the substrate, it offers better fire and thermal protection under severe fire conditions than non-flammable type coatings.

10 Numerous patents and publications, have disclosed intumescent compositions containing one or more polymeric materials in combination with phosphate containing materials and carbonific or carbonic yielding materials.

15 In the patent EP 0 902 062, the intumescent coating compositions can comprise vinyltoluene/acrylate copolymers or styrene/acrylate polymers as a film-forming binder.

20 In the patent US 3 654 190, the intumescent coating contains a solid vinyltoluene/butadiene copolymer associated to a chlorinated natural rubber acting as a char former.

25 In the patent EP 0 342 001, polymeric binder for intumescent coatings comprise copolymers formed of a first monomer in a predominant amount and of a second monomer in a minor amount, said second monomer being a thermally labile co-monomer which is preferably a monomeric aldehyde such as acroleine.

30 In the international patent WO 01/05886, a polymeric binder in an emulsion form is operative to form a film when the composition is allowed to dry; the polymeric binder can be a styrene/acrylate copolymer.

The coatings industry seeks fire retardant coatings which not only meet fire retardancy requirements, but which also possess desirable coating properties. The reactive pigments utilised in the formulation of an intumescent coating are not sufficient in and of themselves to provide desirable coating properties. For example, an intumescent coating must provide all the performance characteristics expected of a conventional coating plus the added benefit of fire retardancy. Incorporating both fire retardance and good coating properties in one system is not straightforward. The combinations of additives such as for formulating an intumescent coating can often result in a formulation possessing both poor coating and poor fire retardancy properties.

It was found that the chemical and physical properties of the binder are critical to the functioning of an intumescent coating. In one hand, the binder should not soften or melt too quickly to permit the formation of a stable char. On the other hand, the viscosity of the binder is correlated with the diffusion and the char formation.

It is therefore desired to provide a polymer binder for intumescent coatings which reduces flame spread during the early stages of a fire and which contributes to improve the char formation and intumescence during the last stage of the fire.

It was shown that the combination of a linear polymer and of a cross-linked polymer as a binder for intumescent coating allows to optimise the char formation and increase the insulating properties of the coatings.

Moreover the inventors have discovered that the more the copolymer contains styrene, the more the interactions with the phosphorus are negative. On the contrary, the more the copolymer contains p-methylstyrene
5 (PMS), the more the interactions with the phosphorus are positive, thus providing a good intumescence.

They have further discovered that the properties of the intumescent compositions according to the invention are correlated with the capacity of the copolymer to
10 react with the phosphor and to the presence of p-methylstyren (PMS) and 2-ethylhexylacrylate (2EHA).

Accordingly the invention provides a copolymer for the use in or as polymeric binder in intumescent coatings, comprising a blend of a newtonian copolymer and
15 of a reticulated copolymer, said newtonian and reticulated copolymers consisting of substituted styrene and substituted acrylate and comprising at least p-methylstyrene (PMS) and 2-ethylhexylacrylate (2EHA).

The invention also provides in another aspect an
20 intumescent fire retardant coating containing the above polymeric binder and a method of forming such a coating.

The reticulated copolymers are chosen in the group comprising the thixotropic copolymers and the pseudo-plastic copolymers.

In the sense of the instant invention, newtonian copolymers refers to copolymers which give a newtonian viscosity profile when dissolved in a solvent, i.e. the viscosity is not shear dependent; thixotropic copolymers refers to copolymers giving a shear thinning solvent solutions, returning to their original state upon standing with time dependency, pseudo-plastic copolymers are copolymers which give a shear thinning solution when dissolved in a solvent.

10 It was found that the ratio between PMS and 2EHA should be of from 100/0 to 50/50, preferably of 90/10, preferably of 80/20 and more preferably of 75/25.

The copolymers used as polymeric binder according to the invention may further contain other substituted styrene like *p*-tert-butylstyrene (PTBS) and/or other substituted acrylates like isobutylmethacrylate (IBMA).

The examples of suitable Newtonian copolymers include Pliolite VTAC-L, Pliolite VTAC-H, Plioway ECH, Plioway Ultra 200, Plioway EC1, all trademarks from
20 ELIOKEM.

The examples of suitable reticulated copolymers include Pliolite AC3H, Plioway ECL, Plioway Ultra G20, Plioway EC-T, all trademarks from ELIOKEM.

The Newtonian and reticulated copolymers are prepared by polymerisation, said polymerisation being effected in a bulk, in a solution, in a suspension or in an emulsion. The best mode is by a conventional emulsion polymerisation.

The polymeric binder may then be formulated by
30 conventional techniques, such as for example by mixing,

with conventional reactive pigments systems, dispersants, plasticizers, defoamers, thickeners, chlorinated paraffin solvents and other additives conventionally employed to prepare the type of desired intumescent coatings (waxes, fillers, fibers, anti-settling agents and the like).

According to the invention, the best mode of forming said polymeric binder comprises the step of (a) dissolving the Newtonian and/or the reticulated copolymers in the solvent or in water, (b) optionally adding the chlorinated paraffin, (c) homogenizing the mixture and adding the additives.

The intumescent coatings according to the invention preferably contain as foam-forming substances ammonium salts of phosphoric acid and/or polyphosphoric acid, more preferably ammonium polyphosphate.

The intumescent coatings according to the invention preferably contain carbohydrides as carbon forming substances, preferably pentaerythritol, dipentaerythritol, tripentaerythritol and/or polycondensate of pentaerythritol.

The intumescent coatings according to the invention may contain halogen or may be halogen free.

The intumescent coatings according to the invention are used in the form of a brushable, sprayable or rollable coating material for protecting different surfaces, preferably steel, wood, electric cables and pipes.

The intumescent coatings according to the invention may be water-based or solvent-based compositions.

The intumescent coatings according to the present invention may be employed in roofing applications to prevent ignition and flame spread, for application onto non-combustible substrates, such as structural steel as
5 in buildings, girders, and the like, vessels, or storage tanks to protect them from weakening upon encountering very high temperatures in fire.

The following examples and the figures are presented to illustrate the invention utilising
10 intumescent coating formulations containing a binder according to the instant invention.

Figure 1 shows the thermal stability of a Newtonian copolymer containing PMS/2EHA (75/25) alone, of ammonium polyphosphate (APP) alone, or of a 60/40 mixture of both
15 (calculated and experimental values).

Figure 2 shows the thermal stability of a Newtonian copolymer containing a styrene/acrylic copolymer alone, of ammonium polyphosphate (APP) alone, or of a 60/40 mixture of both (calculated and experimental values).

20 Figure 3 shows the thermal stability of a copolymer containing a cross-linked copolymer containing PMS/2EHA (75/25) alone, of ammonium polyphosphate (APP) alone, or of a 60/40 mixture of both (calculated and experimental values).

25 Figure 4 shows the thermal stability of a copolymer containing a cross-linked styrene/acrylic copolymer alone, of ammonium polyphosphate (APP) alone, or of a 60/40 mixture of both (calculated and experimental values).

30 Figure 5 illustrates the differences between theoretical and experimental weight loss in TGA for 60/40

blends of various PMS/2EHA (50/50, 75/25 and 100/0) copolymers and APP ($\Delta(T)$ curves)

Figure 6 shows thermal insulation on aluminium plates with intumescent coatings prepared with Newtonian
5 or cross-linked copolymers, said copolymers containing PMS/2EHA (75/25) alone, or PMS/2EHA/acrylic or styrene/acrylic.

Figure 7 illustrates thermal insulation on aluminium plates with intumescent coatings prepared with copolymer
10 containing a blend of Newtonian and cross-linked polymers or with a commercial styrene/acrylic copolymer.

Figure 8 illustrates the values of Rate of Heat Release (RHR) measured with a cone calorimeter after
15 exposition to 35 kW/m² of intumescent coatings prepared with coating 1, coating 2 or coating 4 of example 2.

Example 1: Thermal stability of the polymeric binder

1.1. Measurements

20 The thermal stability of various compositions is measured by thermogravimetric analysis.

Thermogravimetric analyses (TGA) were carried out at 10°C/min under synthetic air or nitrogen (flow rate: 5 x 10⁻⁷ m³/s, Air Liquide grade) using a Setaram MTB 10-8
25 microbalance. In each case, the mass of the sample used was fixed at 10 mg and the samples (powder mixtures) were positioned in open vitreous silica pans. The precision of the temperature measurements was 1.5°C over the whole range of temperatures. The curves of weight differences
30 between the experimental and theoretical TGA curves are computed as follows:

$M_{poly}(T)$: TGA curve of copolymers

$M_{add}(T)$: TGA curve of APP,

$M_{exp}(T)$: TGA curve of copolymer/APP,

$M_{the}(T)$: TGA curve computed by linear combination
between the TGA curves of copolymer and APP,

5 $M_{the}(T) = x M_{poly}(T) + y M_{APP}(T),$

$\Delta(T)$: curve of weight difference:

$$\Delta(T) = M_{exp}(T) - M_{the}(T).$$

The $\Delta(T)$ curve enables the observation of an eventual
increase or decrease in the thermal stability of the
10 polymer related to the presence of the additive.

1.2. Results

The TGA curves are illustrated in figures 1 to 5.

An increase of the thermal stability is obtained
15 with the PMS/2EHA copolymer (figure 1) when compared with
the styrene/acrylic (S/A) copolymer (figure 2).

Similar results are obtained with the cross-linked
copolymers (figures 3 and 4).

The difference between theoretical and experimental
20 weight loss ($\Delta(T)$ curves in figure 5 obtained with
PMS/2EHA copolymers of various ratios show that the
stability increases as the level of substituted styrene
(PMS) increases.

25 Example 2: Preparation of intumescent paints

Different compositions have been prepared. The first
series of paints was prepared without chlorinated
paraffin to visualise the effect of the nature of the
30 polymeric binder on the fire performance. The second
series of paints were prepared with chlorinated paraffin.

Paints were prepared with linear polymer PMS/2EHA, cross-linked polymer PMS/2EHA, linear S/A polymer, cross-linked S/A polymer or comparative commercial S/A copolymer.

- 5 The copolymers were dissolved under high shear in the solvent, then the chlorinated paraffin was added where necessary and after homogenisation the pigments were dispersed in the order described.

The compositions are illustrated in Table 1.

10

2.1. Paints without chlorinated paraffin:

Paint A1: Newtonian PMS/2EHA (75/25) copolymer

Paint A2: Newtonian cross-linked PMS/2EHA (75/25) copolymer

- 15 Paint B1: Newtonian PMS/2EHA/acrylic copolymer (50/14/36)

Paint B2: Newtonian cross-linked PMS/2EHA/acrylic copolymer (50/14/36)

Paint C1: Newtonian styrene/2EHA/acrylic copolymer (50/14/36)

- 20 Paint C2: Newtonian cross-linked styrene/2EHA/acrylic copolymer (50/15/36).

2.2. Paints with chlorinated paraffin

The compositions are illustrated in Table 2.

25

Example 3: Evaluation of thermal insulation

3.1. Measurements

- 30 The temperature profiles are established by measurement of fire resistance with a cone calorimeter. The insulating property of the intumescent coating was tested by measuring the temperature of the coated

substrate submitted to a heat flux of 35 or 75 kW/m². 100 x 100 x 4 mm aluminium panels were coated with the intumescent coatings (800 g/m²) and allowed to dry 48h at 50°C. Samples were exposed to a Stanton Redcroft Cone
5 Calorimeter according to ASTM 1356-90 and ISO 5660 under a heat flux of 35 or 75 kW/m² (50 kW/m² corresponds to the heat evolved during a fire: from V. Babrauskas in *Fire and Mat* (1984), 8(2), 81).

The rate of heat release (RHR) represents the
10 evolution of calorific flow versus time for a given sample surface and is measured using oxygen consumption calorimetry. The data (TCO, TCO₂, TSV and THR) were computed using a home-developed software.

15 3.2. Results

They are illustrated in figures 6 and 7.

The graphs in figure 6 show that the thermal insulation is better when the binder is composed of a combination of linear and cross-linked polymers (paint
20 A2, B2 and C2). When using this combination of polymer, the temperature measured at the back of the coated plate is significantly lower than with the linear polymer as a sole binder. The coatings are particularly efficient when the polymers are prepared from PMS and 2EHA alone
25 (coating A2) or associated to a further substituted acrylate (B2).

Figure 7 shows that after 30 minutes exposure at 35 kW/m², the temperature at the back of the plate
30 remains stabilized at about 310°C when the coating is prepared with the combination of Newtonian and cross-

linked polymers, i.e. about 110°C below the temperature measured with the comparative S/A binder.

Example 4: Fire performance of the intumescent coatings

5

They are measured with paints with chlorinated paraffin and are illustrated in figure 8.

10 All the curves look similar with a first major peak corresponding to the formation of the intumescent structure, followed by a second minor peak or a plateau corresponding to the degradation of the foam and to the formation of a residue, which is stable at high temperature.

15 The rate of heat release (RHR) is maximal for the composition comprising the comparative commercial styrene/acrylic copolymer (200 kW/m²). It is low for the composition comprising the substituted styrene/2EHA copolymers, respectively 139 kW/m² for the PMS/2EHA copolymer and 54 kW/m² for the PMS/PTBS/2EHA copolymer.

20 The RHR obtained with the commercial solvent based paint Unitherm 38091 was measured for comparison and is 186 kW/m².

25 The smoke volumes, CO and CO₂ emission and the total heat release are given in table 2, where the good performance of the substituted styrene/2EHA polymers (paints 1 to 3) as compared to Unitherm 38091.

The low values for smoke, CO and CO₂ emissions obtained with the copolymers as binders according to the invention lead to the protection of the environment.

30

CLAIMS

1. A copolymer for the use in or as polymeric binder in intumescent coatings, comprising a blend of a Newtonian
5 copolymer and of a reticulated copolymer, said Newtonian and reticulated copolymers consisting of substituted styrene and substituted acrylate and comprising at least p-methylstyrene (PMS) and 2-ethylhexylacrylate (2EHA).
- 10 2. A copolymer according to claim 1 wherein the reticulated copolymer is chosen from the group comprising the thixotropic copolymers and the pseudo-plastic copolymers.
- 15 3. A copolymer according to anyone of claim 1 and 2 wherein the ratio of p-methylstyrene and 2EHA is of 100/0 to 50/50, preferably of 90/10, preferably of 80/20 and more preferably of 75/25.
- 20 4. A copolymer according to anyone of claim 1 to 3 further comprising p-tert-butylstyrene (PTBS) and/or isobutylmethacrylate (IBMA).
5. A copolymer according to anyone of claim 1 to 4
25 wherein the copolymers of the blend are obtained by emulsion polymerisation.
6. An intumescent coating comprising a copolymer according to anyone of claim 1 to 5.

7. An intumescent coating according to claim 6 further comprising foam-forming substances, carbon forming substances and other conventional additives.
- 5 8. An intumescent coating according to claim 7 wherein the foam-forming substance is an ammonium salt of phosphoric acid, the carbon forming substance is chosen in the group comprising pentaerythritol, dipentaerythritol, tripentaerythritol and polycondensate
10 of pentaerythritol
9. An intumescent coating according to anyone of claims 6 to 8 which is water based or solvent based.
- 15 10. A method for forming an intumescent coating according to anyone of claims 6 to 9 comprising the step of (a) dissolving the Newtonian and/or the reticulated copolymers in the solvent or in water, (b) optionally adding the chlorinated paraffin, (c) homogenizing the
20 mixture and adding the additives.

TABLE 1

Paint with newtonian resin only

Ingredients	parts
Newtonian resin	4.20
Eastman TXIB	0.9
Bentone SD1	1.02
Tioxide TR92	9.18
Melamine	9.18
Dipentaerythritol	15.61
Exolit AP422	31.33
Solvesso 100	28.57

Paint with newtonian & crosslinked resin

Ingredients	parts
Newtonian resin	3.36
Crosslinked resin	0.84
Eastman TXIB	0.9
Bentone SD1	1.02
Tioxide TR92	9.18
Melamine	9.18
Dipentaerythritol	15.61
Exolit AP422	31.33
Solvesso 100	28.57

TABLE 2

Paint 1	
Ingredients	parts
Newtonian PMS/2EHA resin	6.5
Crosslinked PMS/2EHA resin	2.5
Cereclor S52	3.0
Cereclor 70	6.5
Tioxide TR92	6.0
Dipentaerythritol	8.0
Melamine	8.5
Exolit AP422	26
white spirit 17	23
Solvesso 100	10

Paint 2	
Ingredients	parts
Newtonian PMS/2EHA/PTBS resin	6.36
Crosslinked PMS/2EHA/PTBS resin	0.71
Cereclor S52	2.78
Cereclor 70	4.29
Tioxide TR92	8.08
Dipentaerythritol	12.12
Melamine	13.13
Exolit AP422	22.22
white spirit 17	30.3
Solvesso 100	

Paint 3	
Ingredients	parts
Newtonian Styrene/acrylic resin	8.4
Crosslinked styrene /acrylic resin	2.1
Cereclor 70	8.5
Tioxide TR92	9.5
Dipentaerythritol	7.9
Melamine	7.9
Exolit AP422	26.4
white spirit 17	26.3
Solvesso 100	3.0

comparative Paint 4	
Ingredients	parts
Comparative newtonian Styrene/acrylic resin	9.0
Cereclor 54DP	5.76
Cereclor S52	3.0
Cereclor 70	1.6
Tioxide TR92	6.0
Dipentaerythritol	8.0
Melamine	8.5
Exolit AP422	26.0
white spirit 17	19.6
Solvesso 100	10.0
Bentonite	1.0

Figure 1

Thermal degradation curve of Newtonian PMS/2EHA resin, APP and of the 60/40 w mixtures of the two.

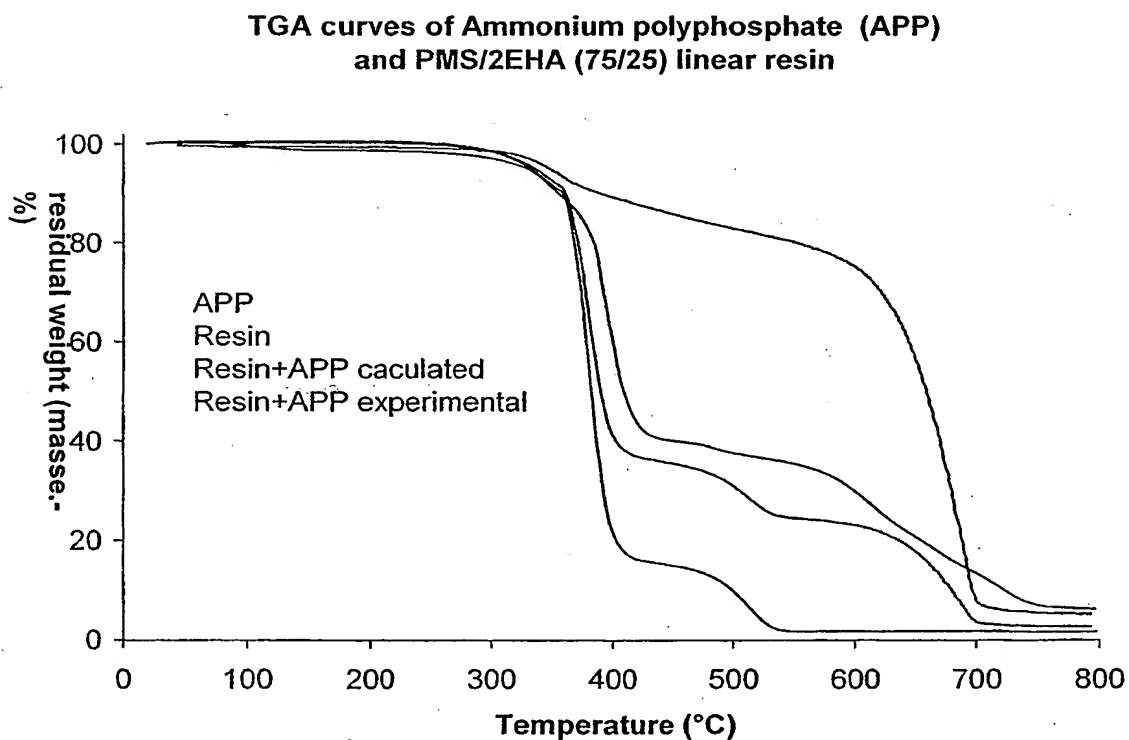


Figure 2

Thermal degradation curve of Newtonian styrene/acrylic resin, APP and of the 60/40 w mixtures of the two.

TGA curves of Ammonium polyphosphate (APP)
and styrene/acrylic linear resin

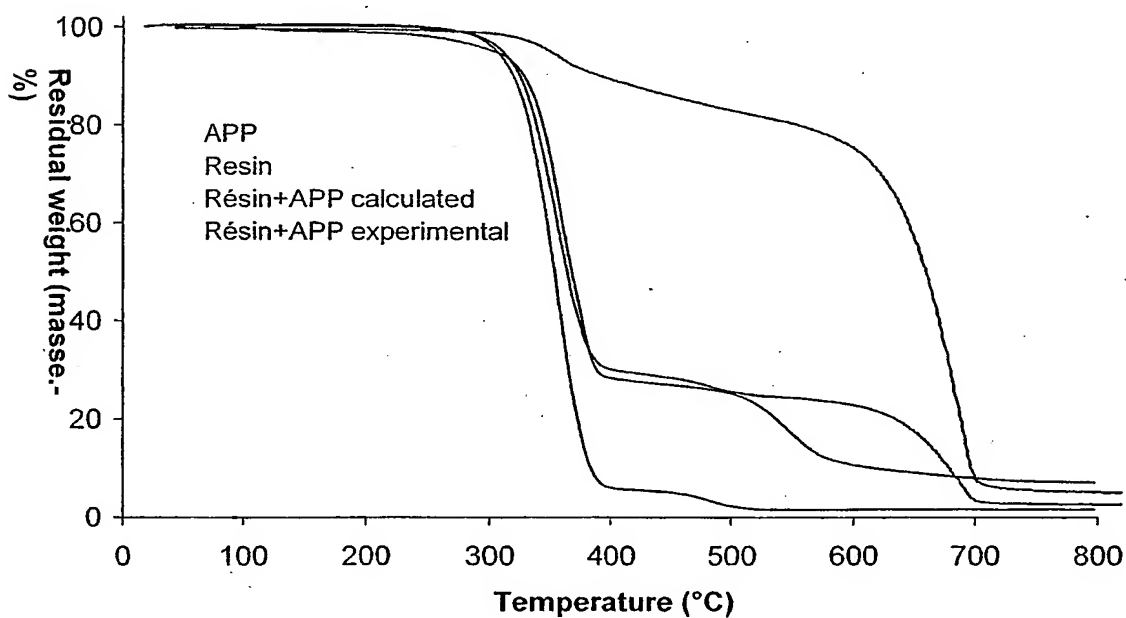


Figure 3

Thermal degradation curve of cross-linked PMS/2EHA resin, APP and of the 60/40 w mixtures of the two.

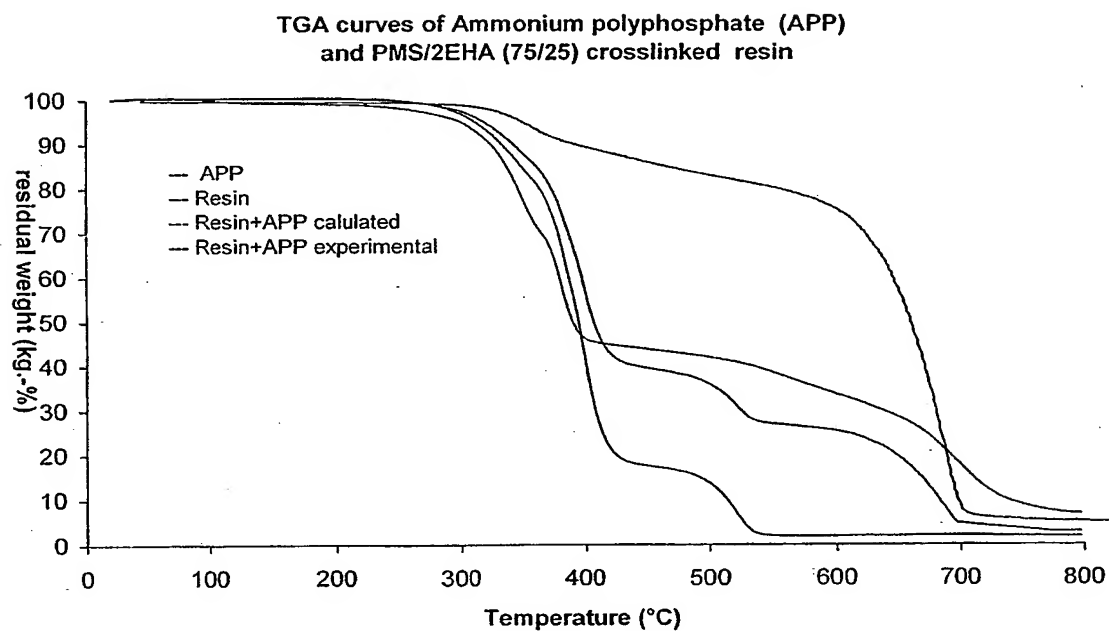


Figure 4

Thermal degradation curve of cross-linked styrene/acrylic resin, APP and of the 60/40 w mixtures of the two.

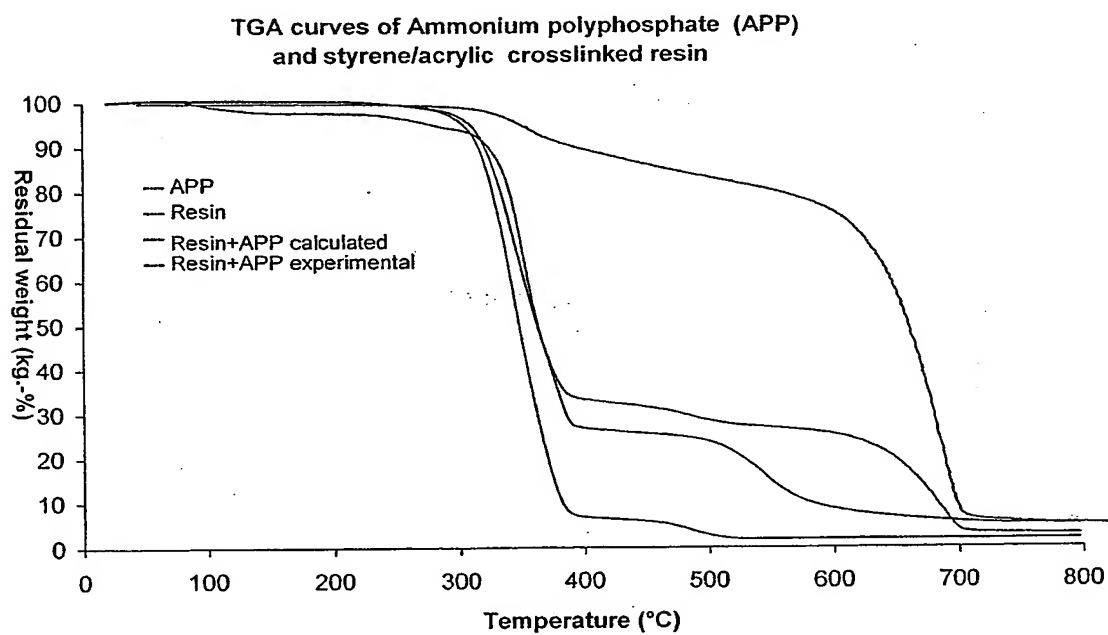
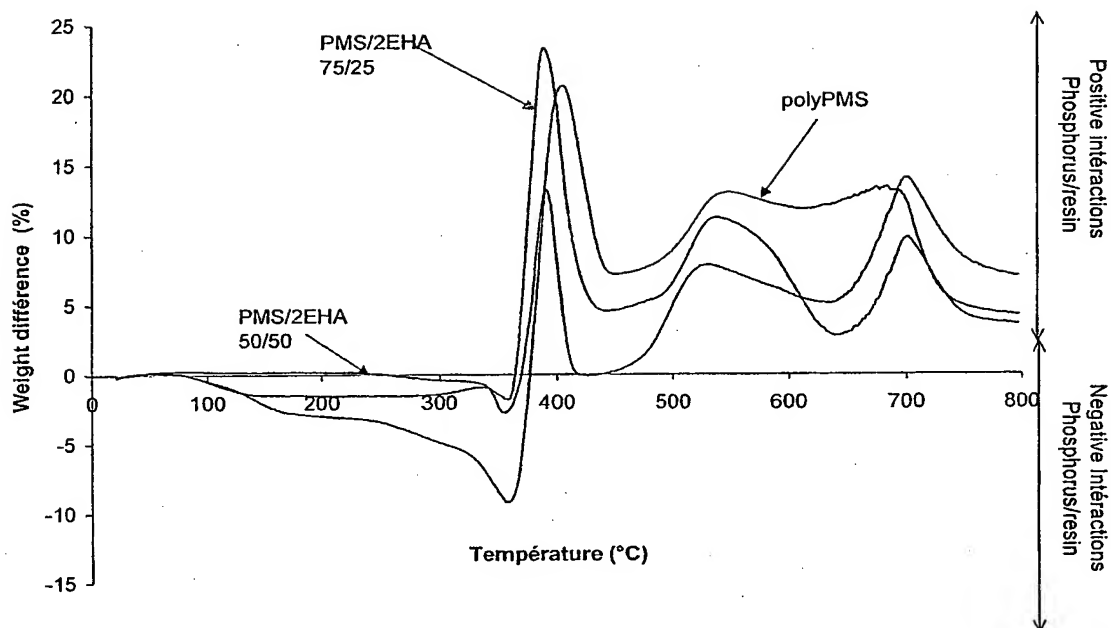
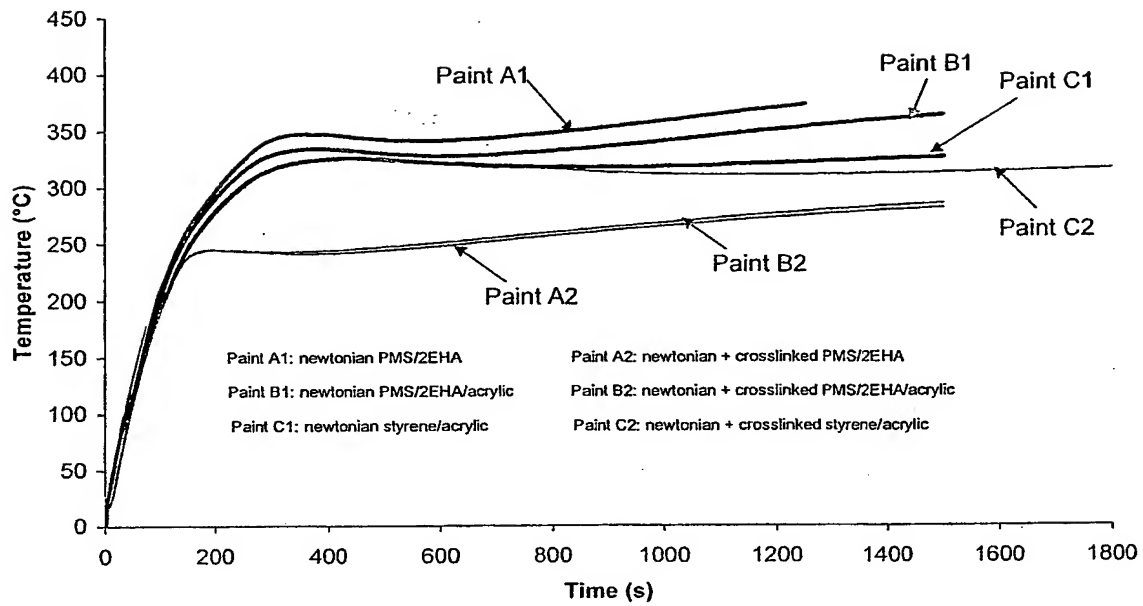


Figure 5



$\Delta(T)$ curves: difference between theoretical and experimental weight loss in TGA for 60/40 blends of various PMS/2EHA resins and APP

Figure 6



Thermal insulation on aluminium plates with intumescent coatings prepared with PMS/2EHA and with styrene/acrylic resins

Figure 7

Thermal insulation on aluminium plates obtained with intumescent coatings prepared with various types of resins

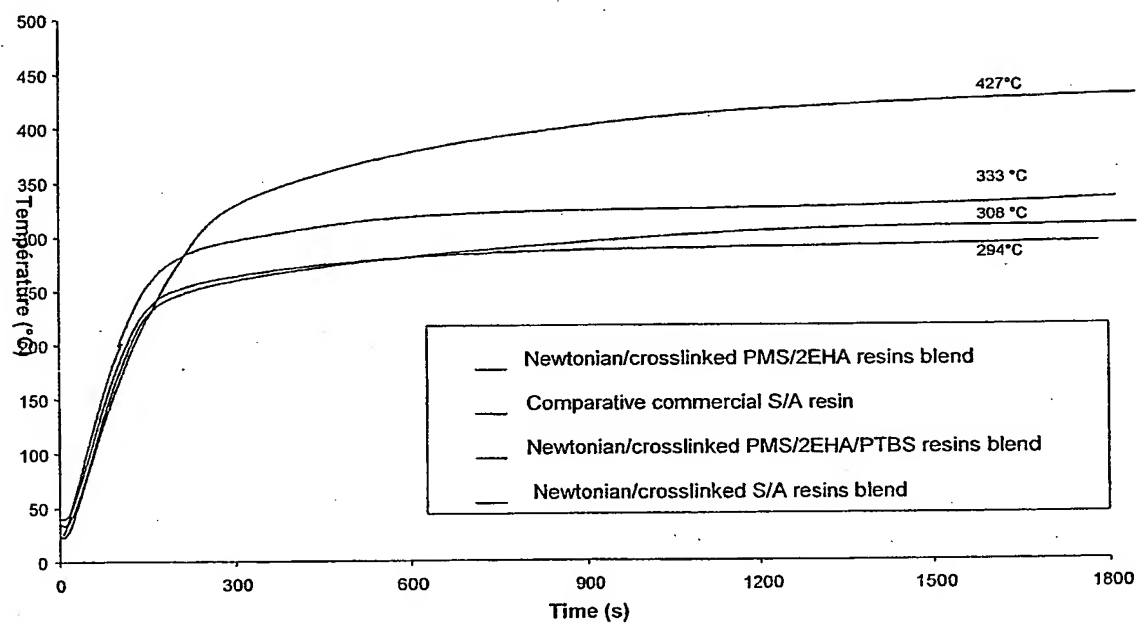
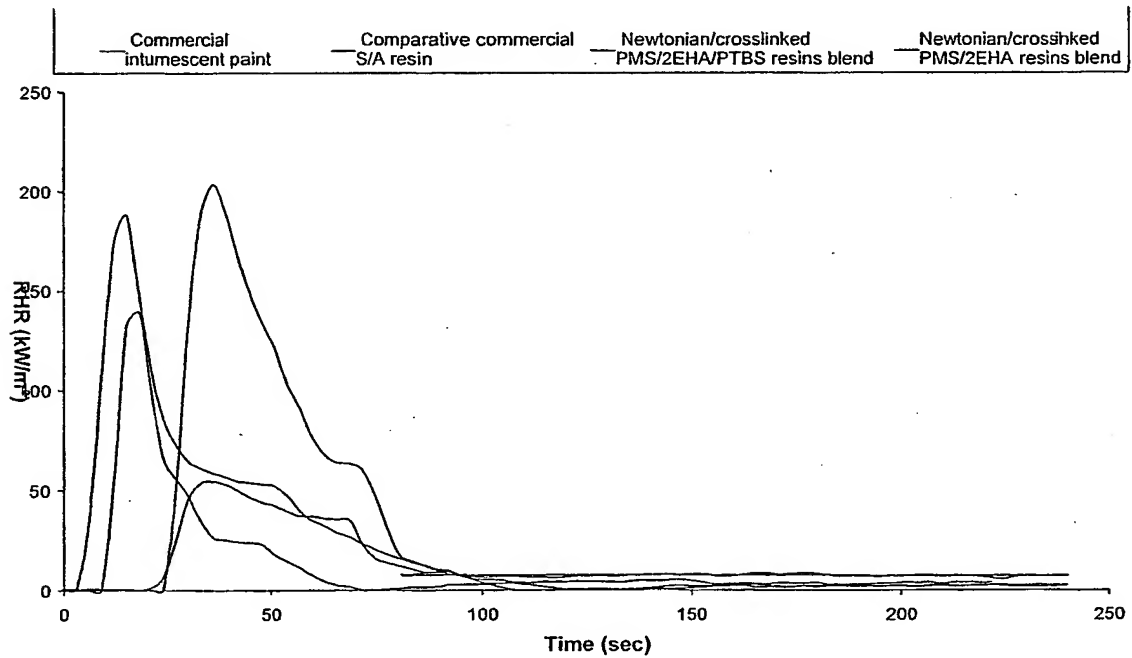


Figure 8

RHR measured with intumescent coatings prepared with various types of resins and exposed at 35 kW/m²



INTERNATIONAL SEARCH REPORT

International Application No

PCT/13 03/06398

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C09D5/18 C08L25/16 C08L33/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09D C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 01/05886 A (GRACE W R & CO ; KUO LAWRENCE J (US); KAUFMAN VLADIMIR (US); MORGAN) 25 January 2001 (2001-01-25) cited in the application claim 7	
A	EP 0 902 062 A (CLARIANT GMBH) 17 March 1999 (1999-03-17) cited in the application claim 5	

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

P-...-3 03/06398

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
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